SPECTRAL ABSORPTIVITY AND THERMAL CONDUCTIVITY OF BGO AND BSO IN MELT AND SINGLE CRYSTAL STATE[1]

S.V.Bykova[2], V.D.Golyshev[2], M.A.Gonik[2,3], V.B.Tsvetovsky[2], E.V. Yakovleva[2].

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[2] Center for Thermophysical Researches "Thermo", Institutskaja Str. 1, 601650, Alexandrov, Russia.
[3] Corresponding author: thermo.ltd@relcom.ru

ABSTRACT

The present work describes the results of researching spectral absorptivity and thermal conductivity of compound oxides $Bi_{12}GeO_{20}$, $Bi_4Si_3O_{12}$ and $Bi_{12}SiO_{20}$ in molten and monocrystalline state. The data on spectral absorptivity was obtained by using the method of placing the sample on the mirror and by the transmission method. To obtain the data on thermal conductivity of crystals, the stationary method of two identical samples was used. The data on thermal conductivity of melts was obtained by a new stationary relative method, in which the crystal, which melt is being investigated, is used as a reference sample. Especial attention is paid to numerical and experimental analysis of sources of errors at measuring these properties at high temperature. The researches have shown that α in the range of transmission band depends on the quality of a crystal. The α value may be in the range from 0.0005 to 0.03 cm^{-1} ($Bi_4Ge_3O_{12}$), and reaches 0.15 cm^{-1} ($Bi_4Si_3O_{12}$). At the same time, α is significantly greater for melts than for crystals and reaches values higher than 150–200 cm^{-1}($Bi_4Ge_3O_{12}$). Thermal conductivity of melts is much smaller then for crystals.

KEY WORDS: crystals; high temperatures; melts; spectral absorptivity; thermal conductivity.

1. INTRODUCTION

High-temperature data on thermal conductivity, λ and spectral absorptivity, α of dielectric single crystals and melts is of great importance for technology of crystal growth from the melt as it allows determining the conditions of heat transfer and the features of interphase kinetics, which provide high perfection of grown crystal. Significance of this data grew as crystal dimensions and number of crystallized compositions increased. In this case selecting the conditions of crystal growth by cut-and-try method becomes too expensive and in order to improve the technology numerical simulation should be used.

For this reason the research of how changing thermophysical and optical properties influence heat and mass transfer with changing of compound oxides composition becomes extremely actual. This fact can be explained in two ways. On the one hand, these crystals have a great number of technical applications. On the other hand, it was shown for $Bi_4Ge_3O_{12}$ [1] that during crystallization of these compound oxides there appears great supercooling on the growing faceted interface. This fact makes them quite attractive for studying fundamental regularities of interfacial kinetics and for verification of modern numerical models, which contain the description of radiative-conductive heat transfer in two-phase media and the description of interfacial kinetics

processes [2].

However there is no data about the properties of the matters, which would allow using the already developed numerical models. On the whole, the aim to obtain high-temperature quantitative data on spectral absorptivity and on thermal conductivity for melts and crystals has been achieved [3-6]. However, these compound oxides have high refraction index n. For example, $n = 2.15$ for Bi_4Ge_3O (BGO) at room temperature. At the same time, the method of placing the sample (a melt) on the mirror used for high-temperature measurements of absorptivity has been already applied, mainly for the matters with low refraction index. Therefore, the influence of high refraction index on the error of absorptivity determination is not studied enough. In order to analyze technological difficulties and to research interphase kinetics processes, one needs besides α data, the data on thermal conductivity close to melting point. The method suitable for study of thermal conductivity close to melting point offered in the work [6] is described in details in [7].

The present article is devoted to analyzing methodical errors made while measuring the mentioned above high temperature properties of dielectrics, and to obtaining the data on thermal conductivity and spectral absorptivity of compound oxides in melt and monocrystalline state.

2. EXPERIMENTAL SETUP AND RESERCH METHODS

2.1. Spectral absorptivity

Absorptivity coefficient α was determined by two techniques. The first technique is a conventional method of transmission measurement for the samples having different thickness. This method was used at the temperature that was 100–200 K less than the melting point. The second one is the method of reflection from the mirror (MR method), on which the sample is located [3].The scheme of the MR method is shown on fig.1.
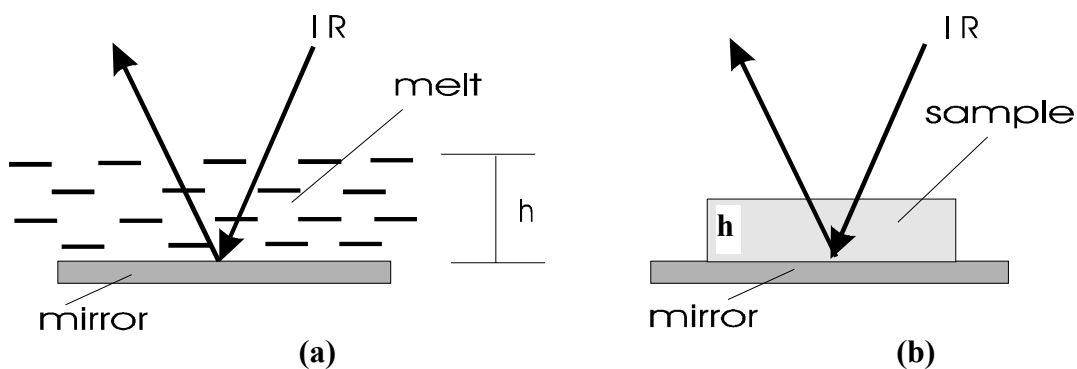
Fig. 1. The schematics of the method of reflection from the mirror: (a) – for the melt, (b) – for the solid samples

This method was used to determine α of a crystal from room temperature up to the temperature that was close to the melting point and that of the melt. Modulated infrared radiation directed on the crystal or the melt sample goes through it, reflects from the

mirror, then again goes through the sample and finally goes to the monochromator and the detector.

The feature of this method is that, in order to measure the intensity of radiation passing through the sample, the optical construction, which is applied for measurement of reflection coefficient, is used. As a result, reflective capacity of the sample-mirror device is actually measured, and, as opposed to the transmission method, the radiation reflected from the sample surface contributes to the signal.

The intensity of the radiation reflected from the sample-mirror system $I = RI_0$ is described for crystals by the formula presented in [6] and for melts by the eq. (1) obtained in [4]:

$$R = r + \left\{ \left[(1-r)^2 r_1 \tau^2 \right] / \left[1 - r_1 r \tau^2 \right] \right\}$$
, (1)

where I_0 is the intensity of the radiation passing through the sample, R is the effective reflective capacity of the sample-mirror layer, $r = (n-1)^2/(n+1)^2$ – is the sample reflection coefficient, r_1 - is the mirror reflection coefficient, $\tau^2 = exp(-2\alpha h)$, h is the sample thickness (fig.1).

If multiple reflections are eliminated, then using the transmission method absorptivity is calculated as (2):

$$\alpha = \frac{ln\ (I_1 / I_2)}{(h_2 - h_1)},$$ (2)

where $I_{1,2}$ is the intensity of the radiation passing through the samples h_1 and h_2 thick accordingly.

Using the MR method for small r value, e.g. without taking into consideration the first and multiple reflections, the similar equation may be used to find α:

$$\alpha = \frac{ln\ (I_1 / I_2)}{2(h_2 - h_1)},$$ (3)

where factor 2 illustrates the fact that the radiation goes through the sample twice. However, in case when the matter, which properties are being measured, have high refraction index, it is necessary to analyze the value of the error caused by eliminating reflections. The results of such investigation are described in part 3.1 of the present work.

2.2.   Measurement of thermal conductivity of single crystals

Effective thermal conductivity λ_{eff} of crystals was determined by the absolute stationary method of two identical plane samples. The scheme of the measurements is presented on fig. 2a.

The samples were made from the single crystal in the form of disks. The diameter of

disks depended on the crystal under study and was in the range from 30 to 70 mm. The ratio of thickness to diameter was in the range of 0.19 to 0.07. To reduce the contribution of heat radiation of the boundaries to the heat transfer, each sample was placed between platinum plates 0.3 mm thick. In its turn, the sample together with the platinum disks was placed between special steel plates (T-disks) served to arrange thermocouples. Temperature was measured with Chromel-Copel thermocouples having electrodes 0.3 mm in diameter in BeO ceramics of diameter 1.5 mm. The main and the guard heater were placed between the internal T-disks (fig.2a). At least, the whole construction was put between two blocks smoothing temperature. In order to reduce the role of contact resistance, the blocks were pressed by load.
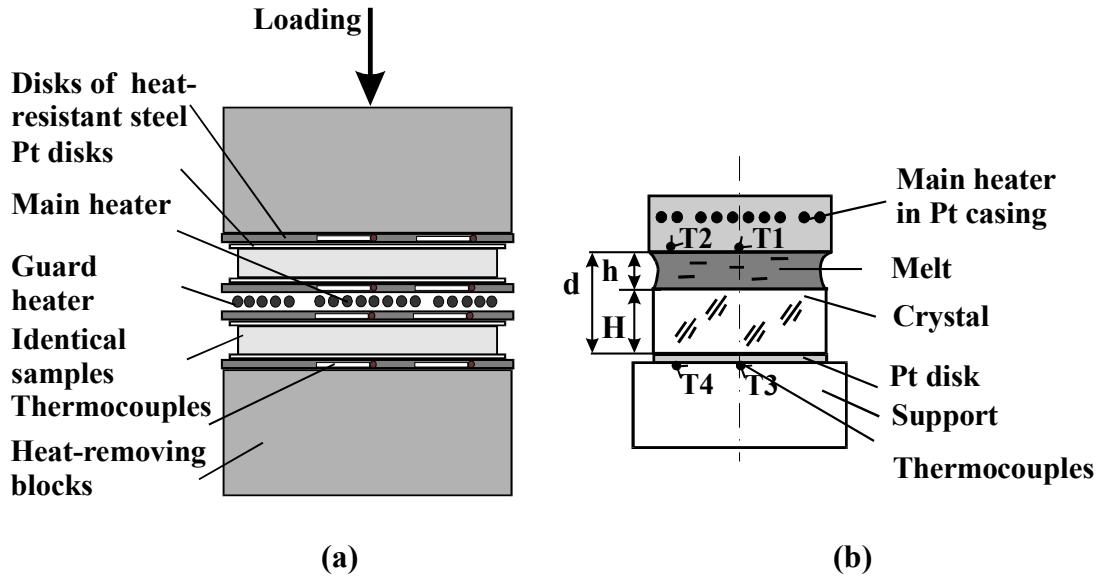

(a) **(b)**

Fig. 2. Schematics of the measuring cell for thermal conductivity of single crystal (a) and melt

The effective thermal conductivity was calculated by the equation:

$$\lambda_{eff}^{cryst} = \frac{q}{\Delta T_1 / H_1 + \Delta T_2 / H_2},$$ (4)

where q is the axial flux through samples of thickness $H_{1,2}$, $\Delta T_{1,2}$ are temperature drops on them.

To determine a real thermal conductivity λ_{cond}^{cryst}, the radiative component q_{rad} should be excluded from the total flux q. Radiative heat flux was determined as a result of solving one-dimensional problem on radiative-conductive heat transfer [8]. For that purpose, the data on spectral absorptivity measured by the techniques described was used. Taking into account that thickness of samples and temperature drops on them are close to each other to measure real thermal conductivity the following equation is to be used:

$$\lambda_{cond}^{cryst} = (q - q_{rad})\frac{H}{\Delta T},$$ (5)

where $H = (H_1 + H_2)/2$, $\Delta T = (\Delta T_1 + \Delta T_2)/2$ are their average values accordingly. One should take into consideration that q_{rad} is rather high due to (besides high temperatures of studies) very high values of refractive index which is in the range of 2.05-2.6 in these crystals [9] influencing the error of thermal conductivity determination.

2.3. Measurement of thermal conductivity of melts

Measurement of thermal conductivity, λ^m of BGO and BSO melts was carried out by the relative stationary method of two samples. The single crystal was used as a reference sample. A scheme of the measurement is given on fig.2b.

The specimens of BGO (in the form of disk 60 mm in diameter and 15 mm thick) and BSO (in form of rectangle with dimensions 80×55 mm^2 and 5.8 mm thick) single crystals were placed between the main heater in the platinum casing and the platinum disks put on the support (Fig. 2b). The temperature of the disk surface $T_{cool} = T_3$ and the casing surface of the main heater $T_{hot} = T_1$ was measured by thermocouples. A portion of the sample of thickness $h \simeq$ 1-2 mm was melted, with a melt being suspended on the heater casing by surface tension forces. Due to small thickness of the melt layer, heating from above and small radial temperature gradient, thermal convection is suppressed. Rayleigh numbers calculated on axial temperature drop depending on melt layer thickness is in the range $Ra_{axial} \sim$ 50-400; Rayleigh number calculated on radial temperature drop is $Ra_{radial} < 1$. Due to small value of ratio $d/D = 0.1$-0.25, as well as to small h, and because of the hot surface is isothermal, the heat flux may be considered as one-dimensional. Therefore effective thermal conductivity of the melt $\lambda_{eff}^{melt} = \lambda_{cond}^{melt} + \lambda_{rad}^{melt}$ may be calculated using the following eq. (6):

$$\lambda_{eff}^{melt} = \lambda_{eff}^{cryst} \frac{T_m - T_{cool}}{T_{hot} - T_m} \frac{h}{H}, \qquad (6)$$

where T_m is the melting point. The exact height of the melted part of the sample and the height of the rest part are determined after quick crystallization and cutting of the sample. Thus thermal conductivity of the melt was found from eq. (7):

$$\lambda_{cond}^{melt} = \lambda_{eff}^{melt} - q_{rad} \frac{h}{T_{hot} - T_{melt}}. \qquad (7)$$

3. DISCUSSION

3.1. Spectral absorptivity

Analysis of systematic errors of measurement and the technique of absorptivity measurement for crystals with high refraction index. While researching compound oxides, the basic error of α measurement arises because of their high refraction index. If we denote the value of absorption coefficient determined in the eq. (2), (3) and (8) as

$\alpha*$, the real value of absorption coefficient resulting from eq. (1), (2) and (3) as α, then the relative error of measurement would be: $\delta(\alpha) = (\alpha* - \alpha)/\alpha$. Fig. 3 shows the dependence of this error on the values r and τ for different methods of absorption coefficient measurement.
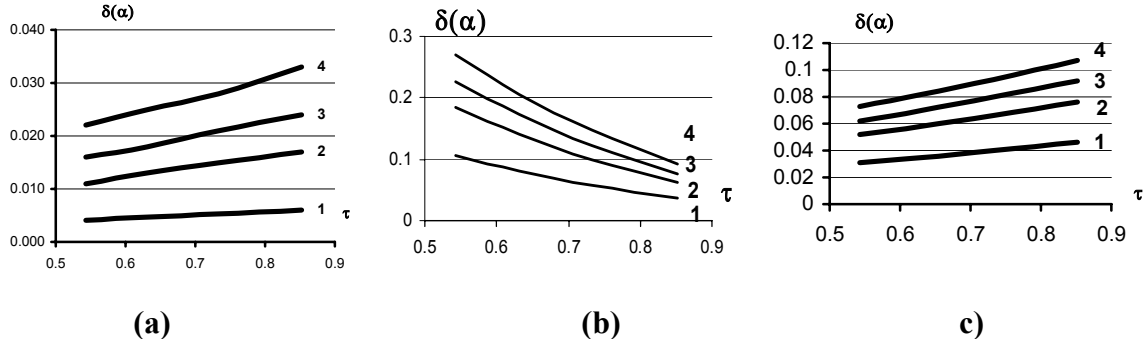
Fig. 3. The dependence of relative error caused by neglect of multiple reflection $\delta(\alpha)$ on the optical thickness $\tau* = 2\alpha h$ of the sample for the reflection coefficient $r = 0.06 - 1$, $r = 0.1 - 2$, $r = 0.12 - 3$, $r = 0.14 - 4$: a) transmission method; b) MR method, the first reflection not taken into consideration; c) MR method, the first reflection taken into consideration.

One can see that the influence of the large value of reflection coefficient on absorptivity is not significant with the use of transmission method (error no more than 4%). In case of MR method, if not taking into consideration the first reflection, the error is almost 30%. To improve the data accuracy while using MR method, the new technique was offered. It suggests measuring the intensity of the radiation reflected from the sample surface (the first reflection, I_r) as well. This value is measured at the wavelengths when the sample absorbs the falling radiation completely. The absorptivity is calculated by the following equation:

$$\alpha = \frac{\ln\left[\dfrac{I_2 - I_r}{I_1 - I_r}\right]}{2 \times (h_2 - h_1)} \qquad (8)$$

As the figure shows, such an approach reduces the error in determination of absorptivity up to 10%.

One more way to increase the data accuracy was used. We added calculated corrections $\Delta\alpha$ to the data obtained by the equations (2), (3) and (8). The formulas of the calculations are different and depend on the measurement methods (9, 10, 11). For example, equation (9) is for transmission method, (10) is for MR method, measurement according to the equation (8) requires the formula (11).

$$\Delta\alpha = \frac{\ln\left[\dfrac{1 - r^2 \times e^{-2\alpha d_2}}{1 - r^2 \times e^{-2\alpha d_1}}\right]}{h_2 - h_1} \qquad (9)$$

$$\Delta\alpha = \frac{\ln\left[\dfrac{\left[r_2 + \dfrac{(1-r_2)^2 \times r_1 \times (\tau_1)^2}{1 - r_2 \times r_1 \times (\tau_1)^2}\right] \times (\tau_2)^2}{\left[r_2 + (1-r_2)^2 \times r_1 \times \dfrac{(\tau_2)^2}{\left[1 - r_2 \times r_1 \times (\tau_2)^2\right]}\right] \times (\tau_1)^2}\right]}{2 \times (h_2 - h_1)} \qquad (10)$$

$$\Delta\alpha = \frac{\ln\left[\dfrac{1 - r_2 \times r_1 \times (\tau_2)^2}{\left[1 - r_2 \times r_1 \times (\tau_1)^2\right]}\right]}{2 \times (h_2 - h_1)} \qquad (11)$$

Absorptivity measurement at high temperature is a very complicated and expensive procedure. That is why optimization (reduce) of expenses is extremely actual problem. We verified the possibility to obtain the data by placing only one sample on the mirror. In this case absorptivity was determined through the ratio I_1/I_2, where $I_1=RI_0$, $I_2 = r_1I_0$ with the use of eq. (3) and the corresponding calculated correction $\Delta\alpha$ to neglect with reflection.

Absorption coefficient of single crystals. Fig. 4 presents spectral absorption coefficient of $Bi_4Si_3O_{12}$, $Bi_{12}SiO_{20}$, $Bi_4Ge_3O_{12}$, $Bi_{12}GeO_{20}$ at room temperature. The study was carried out by using the transmission method of two samples. It is obvious that location and width of the transmission band depends on the type of a crystal. The α value in the region of the transmission band depends on the quality of a crystal. For example, α may change from 0.005 to 0.03 cm^{-1} for $Bi_4Ge_3O_{12}$ and reaches 0.15 cm^{-1} for $Bi_4Si_3O_{12}$ and 0.59 cm^{-1} for $Bi_{12}SiO_{20}$. It is possible to suppose that such large values of absorption coefficient in the transparency region are connected not with physical nature of radiation and environment interaction. The fact is that the growth technology of these crystals is not elaborated enough and these crystals are not rather perfect and high transparent in comparison with that of $Bi_4Ge_3O_{12}$ crystal the growth technology of which is highly developed.
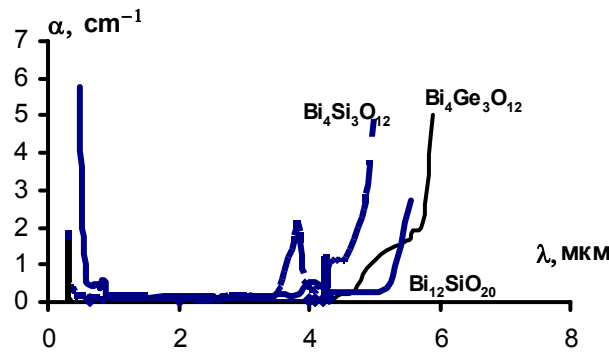

Fig. 4. Absorption coefficient of the single crystals $Bi_4Si_3O_{12}$, $Bi_{12}SiO_{20}$, $Bi_4Ge_3O_{12}$ at room temperature.

In fig. 5 the temperature dependence of $Bi_4Ge_3O_{12}$ absorption coefficient in the near

infrared region of the spectrum is shown. The measurements were carried out in the air atmosphere by RM method. Two samples of different thickness were placed on the platinum mirror. In turns they were exposed to IR-radiation. The temperature on the mirror surface in the area of the beam was measured with the platinum thermocouple. The measurements were done for the type of crystal with absorption coefficient in the transparency field at room temperature $\alpha = 0.03$ cm^{-1}.
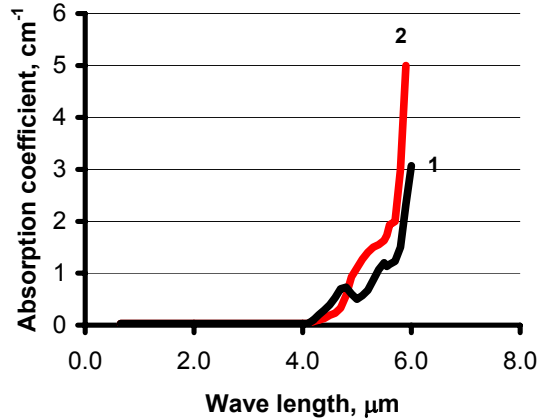
Fig. 5. The temperature dependence of high-frequency edge of lattice transmission band of $Bi_4Ge_3O_{12}$: 1- room temperature, 2 – 900 ^{0}C.

The types of crystals with smaller absorptivity value require the samples with more length. Using in the optical scheme, the setup for measurement of absorptivity of converging rays (Cassegren' scheme) [3] such samples give large error value. That is why these types of crystals have not been studied. Fig. 5 demonstrates that with temperature increase high-frequency edge of lattice transmission band shifts to the short waves area. However this shift is not significant and it cannot be taken into account for calculating radiative-conductive heat transfer. Within the measurements accuracy (transmission value of the sample $\tau^* = 2\alpha h = 0.06$) absorptivity of $Bi_4Ge_3O_{12}$ in the transmission region does not depend upon temperature. The value α remained equal to 0.03 cm^{-1} in the spectrum range from 1 to 4 μm up to the melting point. In order to measure absorption coefficient close to the melting point, RM method was used. The wavelength for investigation was chosen (2 μm in this particular case) and changing of the sample transmission under heating was measured. Melting of the sample was observed by sight, the large value of the melt absorptivity caused considerable reduction of the signal. Thus, the main contribution to the absorptivity in the transparency region is made not by temperature changing, but by the quality of the crystal. In view of this, we can preliminarily conclude that until the crystal growth technology is developed there is no need trying to measure temperature dependence of crystal absorptivity in the transmission region because it is possible to use data for room temperature.

Total instrumental error of α measurement depending on wavelength (the value τ^*) is estimated as 12-20 %. Unaccounted errors of technique are caused by two reasons. The first one is connected with changing of platinum mirror reflection coefficient with time because of interaction between the mirror surface, the sample and the air atmosphere of the furnace. This error was kept under control through measuring 100% line at the

beginning and at the end of experiment at given temperature level. The second error was caused by changing of reflection coefficient of the sample surfaces because of the interaction with platinum mirror and the air atmosphere of the furnace. It was controlled by comparing sample transmission at room temperature before high-temperature measurements and after them.

Absorptivity of the BGO melt. During transition of the single crystal $Bi_4Ge_3O_{12}$ (BGO) into liquid state α value grows considerably from 0.03 cm^{-1} and reaches in the range of 1–4 μm values more than 150–200 cm^{-1}. The measurements were carried out by the RM method. While studying BGO melt, we failed to use the method of reflection from the mirror in the melt in its conventional variant [3], when to obtain several values of melt transmission it is necessary to have several thicknesses of the melt layer on the mirror. The most appropriate conditions of the experiment require the melt layer of such thickness that its absorption was in the range $0.3 < \tau < 0.7$. Because of the large absorption coefficient, the layer of the melt on the mirror should be very thin. But attempts to achieve it by the known way (by changing position of the crucible with the melt relatively to the mirror) brought no result because the melt about 1 mm thick flow down off the mirror. We failed to get the melt less than 1 mm thin and used another way. A plate 0.1 mm thin was cut from the single crystal BGO. The plate was polished on both sides (it should be mentioned that it was impossible to make a polished plate less than 0.1 mm thin). The plate was placed on the platinum mirror. Heating of the plate caused its adhesion with the polished mirror. Due to this fact, when the plate melted the melt remains as a thin layer on the mirror. The exact value of the melt layer thickness was determined after crystallization by means of the thickness of crystallized polycrystal layer. Measurements of intensity of the radiation reflected from the mirror with a thin layer of the melt showed that, even being 0.1 mm thin, the melt absorbs radiation completely. The signal registered by the sensor did not differ (with noise level 0.5 - 1 %) from the signal for a thick layer of the melt. It means that it was determined only by reflection from the melt surface. Thus one can make the following conclusion. Melt transmission allowed maximum only 1% of signal, consequently, $e^{-\alpha 2d} < 0.01$ and finally $\alpha > (ln100)/2d = 200$cm^{-1}.

3.2. Thermal conductivity

Role of contact resistance. The basic error in measurements of λ^{cyrst} by the method described in part 2.1 arises due to the presence of thermal contact resistance, R between thermocouples and the samples and by the wrong value determination of the temperature drop ΔT on the sample. The researches carried out in the work [7], showed that the error of ΔT may reach 15-20%, and it strongly depends on the value of the load on the samples. It was found out that increasing the load for more than 25 kg does not lead to changing of temperature drop; therefore all further measurements were done with such a load.

Since disk processing has essential influence the measurements [7], measuring and platinum disks were polished. At measurement of thermal conductivity of sillenits $Bi_{12}SiO_{20}$ and $Bi_{12}GeO_{20}$ (bismuth silicate and germanate) platinum disks were replaced by nickel disks 0.5 mm thick. These disks during multiple heating and cooling did not

stick to the samples and unlike platinum disks did not deform themselves during assembling-dissembling. Emissivity of nickel in the air atmosphere is much higher than that of platinum. Therefore, radiative flux in $Bi_{12}SiO_{20}$ and $Bi_{12}GeO_{20}$ samples grew in comparison with $Bi_4Ge_3O_{12}$ samples increasing the error of λ^{cyrst} determination.

Nevertheless, the summary error of measurements was successfully reduced because contact resistance of the assembling with nickel disks appeared to be much less (in 40%) than with platinum ones. To improve accuracy of determination of thermal conductivity of the samples, measurements of contact resistance of the assembling itself [7] were specially carried out, when thin (~ 0.2 mm in thickness) disks of Ni were placed instead of studied crystals. Obtained data on R in the total temperature range of thermal conductivity measurements are given in Table 1.

Table 1. Measured values of contact resistance

T (K)	$R\times10^4$ (Km^2/W)	T (K)	$R\times10^4$ (Km^2/W)
304.4	9.81	724.6	6.76
324.8	9.52	869.3	5.73
369.5	8.48	872.1	5.61
545.6	7.44	994.5	5.02
720.5	6.84	997.5	4.70

Decreasing of contact thermal resistance with temperature is connected with increasing of heat transfer in air gaps of assembling by both convection and radiation. To reduce the radiation in the samples, further, while measuring thermal conductivity of $Bi_{12}GeO_{20}$, Pt layer of thickness 50 μm was sputter onto the samples surface.

Thermal conductivity of crystals and melts. The techniques, described in part 2 to measure thermal conductivity of crystals and melts were tested with the use of the
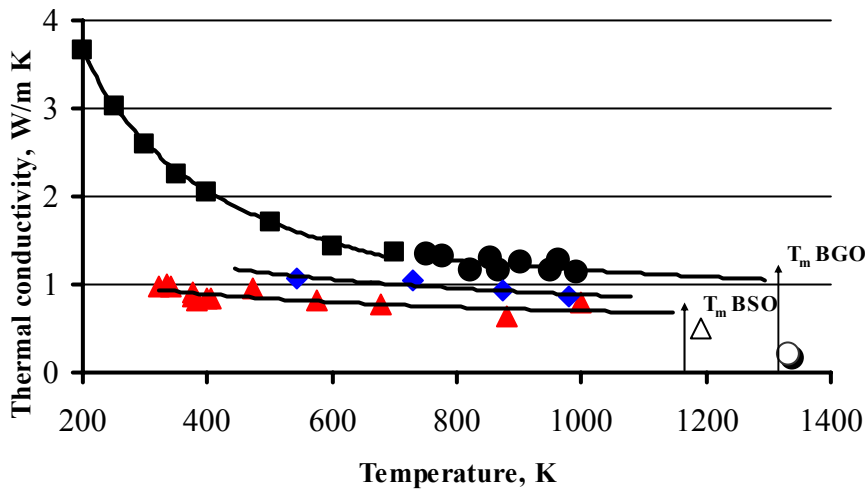

Fig. 6. Thermal conductivity of the single crystals $Bi_4Ge_3O_{12}$ (■ – [10], ● – [6]), $Bi_{12}GeO_{20}$ (◆), $Bi_{12}SiO_{20}$ (▲), and of the melts $Bi_4Ge_3O_{12}$ (○) and $Bi_{12}SiO_{20}$ (△)

matters which are considered to be standard for measuring thermal conductivity under conditions of radiative-conductive heat transfer. These researches for NaCl [7] have shown that the used setup and the techniques provide obtaining the data with 10% accuracy. The results of analyzing thermal conductivity of bismuth germanates and bismuth silicate are presented in fig. 6.

As well as for all dielectrics, thermal conductivity of $Bi_{12}SiO_{20}$ and $Bi_4Ge_3O_{12}$ drops stepwise while melting. The peculiar property of $Bi_4Ge_3O_{12}$ melt is that the value of its thermal conductivity is abnormally low and is close to that of isolators.

It should be noted that the uncertainty of measurement of thermal conductivity of melts by above described technique is rather high ($\sim$ 40-45%). On the one hand, it is connected with the error of calculation of radiation in the crystal that is no less than 18-20% due to our estimations. On the other hand, the applied method is very sensitive to the accuracy of temperature data. Thus, in accordance with eq. (6), the error in 1K, for instance, in melting temperature (T=910 ^{0}C [9]) results in almost 20% error in λ^{cyrst}.

4. CONCLUSIONS

The research has shown that compounds of bismuth oxides with oxides of germanium and of silicon in solid state have relatively low thermal conductivity value at high temperature (about 1 W/m K) and relatively low absorption coefficient. At the same time, the melt has very high value of absorption coefficient and abnormally low value of thermal conductivity.

ACKNOWLEDGEMENTS

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